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Patentanmeldung Nr. | Patent application No. | Demande de brevet n°

03257164.8

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Method for modifying starch or starch derivatives

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Method for Modifying Starch or Starch Derivatives

Technical Field

The present invention relates to a method of modifying starch and starch derivatives in a continuous process. The invention further relates to the use of reactors in such methods.

Background of the Invention

Starch is the principal carbohydrate component of higher plants and has many industrial applications. In the food industry, for example, starch is used, amongst other things, as a texturing agent, gelling agent, thickener and stabilizer. In paper manufacture, starch is used as a sizing agent, for improving printability, surface strength and the solvent-resistance of paper. Starch is also used in the fermentation and textile industries and in the manufacture of adhesives, detergents, cosmetics, pharmaceuticals, emulsifying and dispersing agents, inks and dyes, plastics, coatings and many other commonly used products.

In order to fulfil these roles, however, certain specific properties (such as rheological properties, shear strength, stability, viscosity at different temperatures, gelatinisation, solubility, etc.) may be required. Often, these are not properties associated with native starch. Various methods of starch modification have therefore been developed.

Such methods include hydrothermal treatment, hydrolysis, degradation (dextrinisation, acid-thinning, oxidation), esterification, etherification, stabilistation (e.g. by cross-bonding), etc.

Traditionally, the most successful methods of starch modification on an industrial scale have been based on batch processing in aqueous solutions. Such methods, however, have several innate disadvantages. These include the production of enormous quantities of aqueous effluent, the disposal of which results in a

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considerable burden on production and running costs, and the fact that these methods have to be carried out discontinuously (in batches) which has an adverse effect both on their control and on overall costs.

Several attempts have been made to develop alternative methods for the modification of starch which would overcome these disadvantages. EP710670A1, for example, describes a continuous chemical modification process according to which a starch powder and a reagent are introduced simultaneously into a reactor. A rotating screw within the reactor rapidly creates a fine, dynamic liquid layer, allowing the starch and reagent to interact. This method, however, suffers from several drawbacks. First, due to the speed at which the starch is passed through the reactor, little time is allowed for any reaction to occur (i.e. insufficient contact time between the starch and the reagent is achieved). In addition, under the centrifugation force created by the rotating screw, starch has a tendency to accumulate on the reactor walls. Should the rotating speed be reduced sufficiently to allow for an acceptable contact time and to address the problem of runability, the starch and reagent could no longer be properly mixed, thereby again having a negative effect on reaction levels.

Another example is WO 97/13788 which describes a process for the chemical fluidification of starches carried out under standard plug flow conditions, at temperatures at most equal to 77°C and with reaction times of up to 6 hours. This method also has several disadvantages. First of all, by the very nature of plug flow reactors, very little mixing of materials occurs. As noted above, this will have a negative effect on reaction levels. In addition, with temperatures not exceeding 77°C and because of the static movement of the starch particles through the reactor, they will not be properly dried, even if residence times are increased. Finally, because plug flow reactors in effect mimic batch process conditions, the disadvantages associated with the latter will not be overcome.

There is therefore still a need, in the art, for an improved and more economical method of modifying starch. The present invention provides such a method.

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Summary of the Invention

In a first aspect of the present invention, there is provided a method of modifying starch or starch derivatives comprising: introducing a continuous flow of starch substrate, gas and, optionally, one or more reagents, into a reactor, wherein:

- the starch substrate has a moisture content between 1 and 45% by weight, preferably between 1 and 25% by weight;

- the residence time of the starch in the reactor is between 1 and 60 minutes, preferably between 5 and 45 minutes; and

- the reaction temperature is maintained at between 50 and 220°C, ideally between 100 and 180°C,

characterised in that the starch substrate and the gas are introduced into the reactor in opposing directions.

According to one embodiment, the reactor has a tubular body comprising a shaft upon which is disposed one or a plurality of blades. Preferably, blade or blades will have a tip speed of between 10 and 50 m/s, preferably between 12 and 35 m/s.

The starch substrate may be selected from one or more native starches, starch derivatives, flours, starch suspensions and mixtures of two or more thereof. Preferably, the starch substrate is introduced into the reactor in powder form.

The reagent may be selected from a hydrolysing agent, an oxidation agent, an acid, a dextrinisation agent, an alkylation agent, an esterification agent, an etherification agent, a cross-bonding agent and mixtures of two or more thereof. Preferably, the reagent will be selected from a mineral acid such as citric acid, a peroxide such as hydrogen peroxide (with or without a catalyst such as copper), an oxidising agent and mixtures of two or more thereof.

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According to a preferred embodiment, the reagent is added to the starch substrate before being introduced into the reactor.

In a second embodiment of the present invention, there is provided a method of preparing highly soluble starch comprising: introducing a continuous flow of starch substrate, gas and one or more reagents selected from a mineral acid, a peroxide and an oxidising agent, into a reactor, wherein the starch substrate has a moisture content between 1 and 30% by weight, the residence time of the starch in the reactor is between 5 and 45 minutes and the reaction temperature is maintained at between 80 and 220°C, characterised in that the starch substrate and the gas are introduced into the reactor in opposing directions. Preferably, the starch produced according to this method will be from 70 to 100% soluble in cold water, preferably from 75 to 100% soluble in cold water.

In a third embodiment of the present invention, there is provided the use of a reactor for the modification of starch or starch derivatives, said reactor having a tubular body comprising:

- a shaft upon which is disposed one or a plurality of blades; and

- at least two inlets, one for the introduction of a starch substrate and, optionally, one or more reagents, and one for the introduction of a gas,

characterised in that the inlets are positioned such that the starch and gas are introduced into the reactor in opposing directions.

Description of the Figures

Figure 1 is a schematic representation of a reactor unit according to a possible embodiment of the present invention.

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Detailed Description of the Invention

The present invention provides a method of modifying starch or starch derivatives. The term "starch derivatives" refers to any molecule produced by a modification or series of modifications - physical, chemical and/or genetic - to starch. Accordingly, starch derivatives include (but are not limited to): enzyme or acid hydrolysed starches (such as maltodextrins, glucose syrups and hydrolysates); degraded starches (e.g. starches degraded by heat, oxidation, catalysts or acidification such as roast dextrin and thin-boiling starch); pre-gelatinised starches; starch esters (such as starch n-octenyl succinate); starch ethers; cross-bonded starches; retrograded starches; bleached starches; cationised or anionised starches and alkali treated starches. For simplicity's sake, any references herein to starch will be understood to include both native starch and starch derivatives.

The term "starch substrate", by contrast, refers to the actual product which is introduced into the reactor in a first step of the present method. It may be any starchy material suitable for use in a tubular reactor (such as flour, a starch suspension or a starch cake). The substrate may comprise one or more native starches, one or more starch derivatives or a mixture thereof. Preferably, it will consist of purified starch and/or starch derivative(s). The starch itself can be of any desired origin (potato, wheat, corn, rice, tapioca, pea, barley, etc.) and can be waxy or not. The substrate may be used in combination with one or more natural or synthetic polymers (such as cellulose) and/or one or more organic or inorganic compounds. Alternatively, it can be mixed to a buffer before being introduced into the reactor. It will preferably be in powder form and will have a moisture content between 1 and 45% by weight, preferably between 1 and 25% by weight, even more preferably between 3 and 25% by weight at its point of entry into the reactor. Moisture levels can be controlled within the reactor if necessary (for example by adding water with the gas phase and/or by controlling reaction temperature). Preferably, moisture levels of 0-15% by weight will be obtained at the reactor outlet.

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The reactor, as defined herein, is a reactor having a tubular, preferably cylindrical, body within which is positioned a rotating shaft. The shaft is provided with one or a plurality of blades. By "one or a plurality of blades", it is not intended to limit the reactor to any particular construction. Indeed, the blade or blades may just as well take the form of a number of separate paddles or of a single, helical blade disposed around the shaft in the manner of a screw thread. The blade or blades will preferably have a tip speed between 10 and 50 m/s. Ideal rotating speeds will depend on the size of the reactor. Thus, for a large reactor (i.e. a reactor having a diameter of 1m or more), tip speed should preferably be between 12 and 35 m/s, even more preferably between 15 and 25 m/s. For a small reactor (i.e. a reactor having a diameter of less than 1m), tip speed may be from 10 to 50 m/s, preferably from 12 to 45 m/s and even more preferably from 15 to 35 m/s.

In use, the blades will convey the starch substrate from an inlet at one end of the reactor to an outlet at the other end in a continuous manner. As will be appreciated by the skilled person, the term "continuous" here distinguishes the present method from a batch process but dos not necessarily imply that the flow of starch into and through the reactor is uniform or indeed constant.

The temperature at which the reaction occurs will preferably be between 50 and 220°C. Preferably, it will be set at between 80 and 220°C, even more preferably at between 100 and 180°C. Ideally, the temperature will be set at between 100 and 160°C. Residence time within the reactor will be between 1 and 60 minutes, preferably between 5 and 45 minutes and, even more preferably, between 10 and 30 minutes. Of course, the exact residence time will be determined for each reaction, taking into account various variable factors (e.g. nature of substrate, temperature of reactor, quantity and nature of reagent, speed of rotation, etc). Ideally, both moisture and pH conditions within the reactor will be controlled.

As mentioned above, the reactor comprises an inlet for the starch substrate. It also comprises a gas inlet positioned such that the starch substrate and gas are introduced into the reactor in opposing directions. Of course, the substrate and gas inlets do not

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necessarily have to be on geometrically opposing sides of the reactor, provided that they are sufficiently separated and angled such that, in use, the substrate flow and gas flow run counter-current to each other.

These counter-current flows results in better mixing of the starch substrate with any eventual reagents and in better control of residence times (i.e. the starch is prevented from passing too quickly through the reactor). Because of the resulting turbulence, substrate particles will come into contact more often with the heated reactor wall. Particle temperature will therefore increase more quickly thus accelerating the reaction rate. The counter-current flows also provides an efficient method of transporting reactants (including moisture) through the reactor with relatively small amounts of gas whilst maintaining the substrate particles in an aerated suspension. This results in increased reaction efficiency and therefore reduced costs. In addition, it avoids the usual drawbacks associated with the use of batch reactors and of with the continuous reactors of the prior art (e.g. runability).

The gas used to create the counter-current may be any gas but will preferably be air, nitrogen, carbon dioxide, an inert gas, controlled oxygen or a mixture of two or more thereof. It may include reagents such as oxidants (e.g. ozone), amines, neutralising agents or additives capable of modifying or controlling reaction conditions (e.g. pH and/or moisture). It may also be heated before entry into the reactor.

The reactor may comprise one or more additional inlets for the introduction, if desired, or one or more reagents (enzyme, catalyst, etc.). The use of a reagent is not always necessary as the modification may simply consist of a physical modification (e.g. by heating). However, if a reagent is used, it can be selected, for example, from any one or more of: a hydrolysing agent (such as α-amylase, β-amylase, glucoamylase or pullulanase), an oxidation agent (such as sodium hypochlorite), an acid such as an acid-thinning agent (e.g. H_2SO_4 or H_3PO_4), a dextrinisation agent (such as HCl), an alkylation agent (such as an alkali hydroxide), an esterification agent (such as acetic anhydride, vinyl acetate or n-octenyl succinate anhydride), an etherification agent (such as propylene oxide) or a cross-bonding agent (such as phosphorous oxychloride,

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sodium trimetaphosphate or mixed anhydride of acetic and adipic acid). This is of course not an exhaustive list as the selection of a reagent will depend on the type of modification to be achieved. A skilled person will be able to choose which reagent or reagents should be used in view of the type of reaction to be performed.

For example, if it is desired to increase the solubility of starch, the reagent will preferably be a mineral acid (such as citric acid), a peroxide (such as hydrogen peroxide) and/or an oxidising agent. It has indeed been found that, using the method of the present invention, highly soluble starches can be produced in an economical way on an industrial scale. In particular, the method of the present invention can be used to produce starches or starch derivatives which are 70-100%, preferably 75-100% soluble in cold water (i.e. in water having a temperature of no more than 50°C).

The reagents, if used, can be added in the form of a solution, powder or gas (preferably in the form of a solution) and in concentrations of 0.001-20% by weight. Preferably, they will be added in concentrations of 0.001-10% by weight and, even more preferably, in concentrations of 0.01-3% by weight. Again, the skilled person will be able to determine the appropriate concentration of reagent needed depending, for example, on the quantity of substrate to be modified, the desired level of modification, the nature of the reagent being used, etc.

As noted above, any eventual reagent or reagents can be introduced into the reactor via one or more separate inlets to that used for the starch substrate. Alternatively, the reagent(s) and the starch could be introduced via the same inlet. In both the above cases, the reagent and starch will be mixed within the reactor. However, in a preferred embodiment, reagent and starch will be mixed before being introducing into the reactor. Thus, the method of the present invention may contain an initial step comprising forming a premix by combining reagent(s) and starch substrate. The premix can then be introduced into the reactor via a single inlet.

If the reagent is to be added to the starch substrate before being introduced into the reactor, the blending step can be carried out in a mixing chamber linked to the reactor.

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Thus, the reactor so far described may be part of a larger unit ("reactor unit") comprising both downstream and upstream components. Downstream components could include, for instance, the already mentioned mixing chamber or a pre-modification chamber (e.g. if the starch substrate needs to undergo an initial modification before being introduced into the reactor, for example by cooking or by a hydrothermal treatment) while upstream components could include, for instance, a drying chamber, a recycling element or one or more further reactors. According to one embodiment, the unit as a whole may include more than one reactor according to the present invention (e.g. if several different modifications are necessary or if a longer residence time is desired). Thus, product issuing from one reactor can be passed (directly or indirectly) to one or more further reactors. When there is more than one reactor according to the present invention, they will preferably be disposed in series.

A possible reactor unit, in accordance with the present invention, is illustrated in Figure 1 in which (1) represents a counter-current reactor, (2) represents an optional finishing reactor, (3) represents the shaft-rotating motor, (4) represents an optional dust separator, (5) represents an optional condensator and (6) represents a heat exchanger. Starch substrate is introduced into the reactor via inlet (a). Gas (with or without reactant and/or water added at (f)) is introduced via inlet (c) and exits the reactor via outlet (d). It may then leave the reactor unit via exhaust (k) or be recycled to the heat exchanger via inlet (j). Modified starch product leaves the reactor via outlet (b). After optional further processing, the product leaves reactor (2) via outlet (e). Condensate is released from the condensator via outlet (g). Alternatively, dust gathered at (4) may be recycled to the reactor at inlets (h) and/or (i).

The present invention also provides for the use of a reactor or reactor unit as described for the modification (hydrolysis, degradation, esterification, etherification, stabilistation, etc.) of starch or starch derivatives.

The invention will now be illustrated by the following, non-limiting examples.

<u>Example 1</u>

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Corn starch and 30 mEq/kg HCl are blended in a Lödige mixer and dried such that a final moisture content of 15% by weight is obtained. The blend is then introduced into the reactor in a continuous flow. A counter current of gas at 180°C is introduced simultaneously. The jacket temperature of the reactor is maintained at 175°C such that the starch product reaches a temperature of 110-120°C. Residence time of the starch substrate in the reactor is 5 minutes. The product obtained at the outlet of the reactor has a significantly lower paste viscosity than untreated starch.

Example 2

Corn starch and 80 mEq/kg HCl are blended in a Lödige mixer and dried such that a final moisture content of 15% by weight is obtained. The blend is then introduced into the reactor in a continuous flow. A counter current of gas at 180°C is introduced simultaneously. The jacket temperature of the reactor is maintained at 220°C such that the starch product reaches a temperature of 160°C. Residence time of the starch substrate in the reactor is 30 minutes. The product obtained at the outlet of the reactor has a low moisture content, low viscosity and is an increased cold water solubility.

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Claims

1. A method of modifying starch or starch derivatives comprising: introducing a continuous flow of starch substrate, gas and, optionally, one or more reagents, into a reactor, wherein the starch substrate has a moisture content between 1 and 40% by weight, the residence time of the starch in the reactor is between 1 and 60 minutes and the reaction temperature is maintained at between 50 and 220°C, characterised in that the starch substrate and the gas are introduced into the reactor in opposing directions.

2. A method according to claim 1 wherein the reactor has a tubular body comprising a shaft upon which is disposed one or a plurality of blades having a tip speed of between 10 and 50 m/s, preferably between 12 and 35 m/s.

3. A method according to claim 1 or claim 2 wherein the starch substrate has a moisture content of between 1 and 25% by weight.

4. A method according to any one of the preceding claims wherein the starch substrate is selected from one or more native starches, starch derivatives, flours, starch suspensions and mixtures of two or more thereof.

5. A method according to any one of the preceding claims wherein the starch substrate is introduced into the reactor in powder form.

6. A method according to any one of the preceding claims wherein the reagent is selected from a hydrolysing agent, an oxidation agent, an acid, a dextrinisation agent, an alkylation agent, an esterification agent, an etherification agent, a cross-bonding agent and mixtures of two or more thereof.

7. A method according to any one of the preceding claims wherein the reagent is selected from a mineral acid, a peroxide, an oxidising agent and mixtures of two or more thereof.

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8. A method according to any one of the preceding claims wherein the one or more reagents are added in an amount between 0.001 and 20% by weight.

9. A method according to any one of the preceding claims wherein the one or more reagents are introduced into the reactor in the form of a solution, powder or gas.

10. A method according to any one of the preceding claims wherein at least one of the one or more reagents is added to the starch substrate before being introduced into the reactor.

11. A method according to any one of the preceding claims wherein the residence time of the starch in the at least one reactor is between 5 and 45 minutes.

12. A method according to any one of the preceding claims wherein the reaction is maintained at a temperature between 100 and 180°C.

13. A method according to any one of the preceding claims wherein the gas introduced into the reactor is selected from: air, nitrogen, carbon dioxide and a mixture of two or more thereof.

14. A method of preparing highly soluble starch comprising: introducing a continuous flow of starch substrate, gas and, one or more reagents selected from a mineral acid, a peroxide and an oxidising agent, into a reactor, wherein the starch substrate has a moisture content between 1 and 30% by weight, the residence time of the starch in the reactor is between 5 and 45 minutes and the reaction temperature is maintained at between 80 and 220°C, characterised in that the starch substrate and the gas are introduced into the reactor in opposing directions.

15. A method according to claim 14, wherein the reaction is carried out under controlled moisture and pH conditions.

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16. A method according to claim 14 or claim 15, wherein the highly soluble starch is from 70% to 100% soluble in cold water.

17. Use of a reactor for the modification of starch or starch derivatives, said reactor having a tubular body comprising:

- a shaft upon which is disposed one or a plurality of blades; and
- at least two inlets, one for the introduction of a starch substrate and, optionally, one or more reagents, and one for the introduction of a gas, characterised in that the inlets are positioned such that the starch and gas are introduced into the reactor in opposing directions.

18. Use according to claim 17 wherein the blade or blades have a tip speed of between 10 and 50 m/s, preferably between 12 and 35 m/s.

19. Use according to claim 17 or claim 18 for the hydrolysis, degradation, oxidation, acid degradation, dextrinisation, bleaching, etherification, esterification, cross-bonding, alkylation or acetylation of starch and/or starch derivatives.

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Method for Modifying Starch or Starch Derivatives

Abstract

A method of modifying starch or starch derivatives comprising: introducing a continuous flow of starch substrate, gas and, optionally, one or more reagents, into a reactor, wherein the starch substrate has a moisture content between 1 and 40% by weight, the residence time of the starch in the reactor is between 1 and 60 minutes and the reaction temperature is maintained at between 50 and 220°C, characterised in that the starch substrate and the gas are introduced into the reactor in opposing directions.

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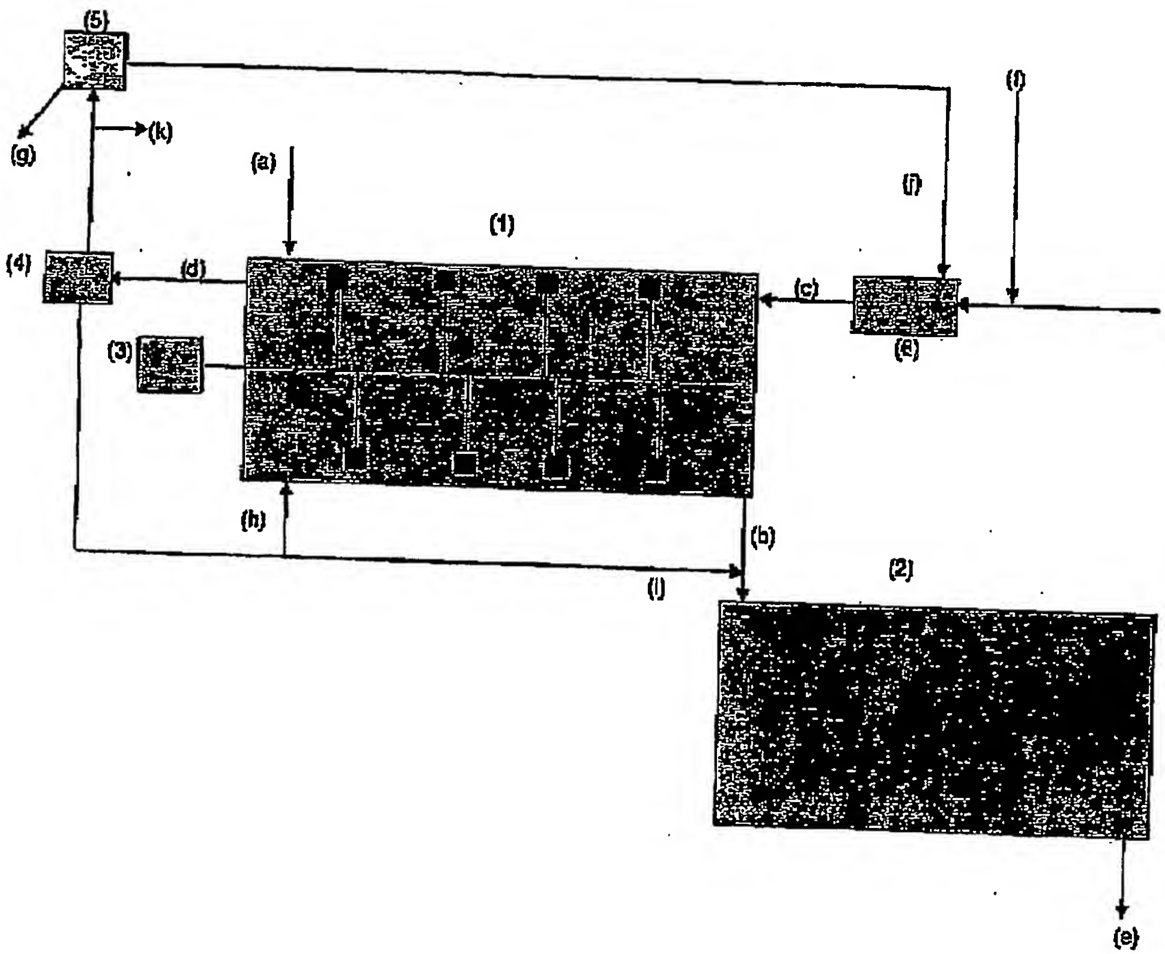
Figure 1



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